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DEPARTMENT OF COMMERCE

UNITED STATES BUREAU OF MINES
SCOTT TURNER, DIRECTOR

INFORMATION CIRCULAR

SELENIUM AND TELLURIUM

BY

R. M. SANTMYERS

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By R. M. Santmyers[2]

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INTRODUCTION

Selenium and tellurium, together with oxygen and sulphur, form the oxygen family of elements. They are all bivalent. The specific gravities, melting points, boiling points, etc., of these four elements increase with increasing atomic weights. The following table shows the gradation in physical properties from oxygen at one end of the series to tellurium at the other.[3]

Properties of the oxygen - sulphur family

	Oxygen	Sulphur	Selenium	Tellurium
Atomic weight	16	32.07	79.2	127.5
Melting point	-227°	114° - 115°	170° - 217°	452° - 454°
Boiling point	-183°	448°	688°	1390°
Specific gravity (solid)	1.43	1.96 - 2.06	4.28 - 4.80	5.93 - 6.4
Atom. vol. (approx.)	11	16	18	21
Color of solid	Pale blue	Yellow	Reddish brown	Black
Heat of union with (hydrogen (cals.)	69.0	4.8	-25.1	-34.9

1 The Bureau of Mines will welcome reprinting of this article, provided the following footnote acknowledgment is used: "Reprinted from U. S. Bureau of Mines Information Circular 6317."

2 Mineral specialist, rare metals and nonmetals division, U. S. Bureau of Mines.

3 Mellor, J. W., Modern Inorganic Chemistry. London, 1928, pp. 461 - 462.

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Selenium and tellurium lie closer even than sulphur to that ill-defined border line between the metals and nonmetals. All four elements exhibit allotropism. Oxygen occurs most abundantly, sulphur and then selenium next, and tellurium the least abundantly. They all produce hydrogen compounds of the same type, but while the hydrogen compounds of sulphur, selenium, and tellurium are fetid smelling gases at ordinary temperatures, hydrogen oxide (water), H_2O, is a colorless, odorless liquid.

Selenium and tellurium are essential constituents of several minerals, and tellurium is found native. The commercial source of both elements, however, is the relatively minute amounts present as impurities in various ores, and recovered as by-products in the refining of copper and lead and from the manufacture of sulphuric acid from pyrite. The quantities recovered in this manner could be largely increased if the demand warranted the slight additional expense of working up certain residues.

In the United States alone the potential production of selenium, virtually as a by-product of major metallurgical operations, has been estimated at 400,000 to 450,000 pounds annually, while that for tellurium was from 100,000 to 150,000 pounds. Because of restricted present-day demand, the sales, especially of tellurium, represent only a small fraction of the potential output.

Both of these elements have possible new uses, and the research that has been actively in progress for many years is likely to uncover additional fields of employment. Tellurium, especially, may find a market for use as an alloy with a few of the base metals such as copper, lead, iron, and aluminum. New uses are being continually found for both selenium and tellurium in the medicinal and chemical industries, but the amounts required, even in the aggregate, have hitherto been too small to have much effect upon sales. Compounds of tellurium, for example, have been recommended in connection with certain blood and tissue diseases.[4]

At present the only possible use for selenium which may create a much larger demand for the element is its use in the rubber industry, but even in this field considerable additional research may be necessary.

SELENIUM

Description and Properties

Selenium closely resembles both sulphur and tellurium in its properties and, like sulphur with which it is isomorphous, exists in at least three allotropic modifications: (1) Amorphous selenium is formed as a finely divided brick-red precipitate when a solution of selenious acid is saturated with sulphur dioxide gas. This form of selenium is said to be soluble in carbon disulphide. (2) Vitreous selenium is formed when the amorphous variety is heated to 217° C. and rapidly cooled. It is a black, brittle, and glassy mass with a highly lustrous

4 Lenher, Victor, Occurrence, Chemistry and Uses of Selenium and Tellurium, A.I.M. M. E. Trans. New York, No. 1198-N, Feb., 1923, 20 pp.

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surface. It has no definite melting point but will soften at 100° C. and be completely molten at 250° C. Similar to the amorphous modification, vitreous selenium will not carry electricity, and in all selenium cells, the selenium must be converted to the metallic modification before the cell will function. The specific gravity of vitreous selenium is from 4.2 to 4.5. (3) Metallic selenium is obtained on heating vitreous selenium; if vitreous selenium is kept at 210° C. for some time, the mass suddenly melts, the temperature rising to 217° C., and metallic selenium solidifies in a metallic, granular, crystalline form. The same phenomenon takes place if the vitreous selenium is kept heated at 100° C. for several hours. Metallic selenium occurs in steel-gray, hexagonal crystals having a specific gravity of 4.8 and a melting point of 217° C. It is the only modification of selenium which will conduct electricity.

The first of these forms may include amorphous selenium and semicolloidal red amorphous selenium; the three are regarded as belonging to one allotropic modification and are sometimes known as "liquid" selenium. The second, the monoclinic or red crystalline selenium, also exists in two modifications, both of which belong to the monoclinic system.

Selenium boils at 700° C., giving a yellow vapor which condenses to "flowers of selenium." It burns in air, dissolves in both sulphuric and nitric acid, and unites with metals to form selenides.

The element itself is odorless and tasteless but when heated it produces an odor resembling carbon disulphide and usually described as that of putrid horse-radish. It burns with a reddish-blue flame. In cold concentrated sulphuric acid it dissolves with a fine green color, forming selenosulphur trioxide ($SeSO_3$), which is precipitated, however, when the solution is diluted with water.

A unique property of selenium and the one upon which its important use depends is that of the lowering of its electrical resistance upon exposure to light. The action is produced principally by the red rays and is proportional to the intensity of the light. The change is not instantaneous and for this reason can not compete favorably with the potassium photoelectric cell, which, though considerably more costly, is instantaneous as regards its recovery after exposure to light.

USES

Selenium in metallic form has long been characterized by its unique action toward light. Its conductivity of an electric current varies so greatly when brought from the dark into the light that this peculiar property, varying as it does in direct proportion to the intensity of the light, has caused the development of the selenium cell.

Apart from this use, which employs only a minute fraction of the output of selenium, there are several other uses which make this metal a valuable substance in industry. Among these are its use for flameproofing switchboard cables, as a vulcanizing and accelerating agent in the manufacture of rubber, and as a colorizer and decolorizer in the glass and pottery industries.

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The selenium cell has received considerable attention for many years. Its action toward light and the resulting effect upon its resistance was discovered by W. Smith in 1873, being brought about through experiments with it in connection with testing signals during submersion of long submarine cables.

Early experiments did not place selenium in a very favorable light for the purpose required, for although the resistance was all that was needed - some of the bars giving 1,400 megohms absolute - yet there was a discrepancy in the tests and seldom did different operators obtain the same result. The experiment was carried out with several bars of selenium varying in length from 5 to 10 centimeters with a diameter of 1 to 1½ mm. Each bar was hermetically sealed in a glass tube, and electrical contact was provided through platinum wires sealed at each end of the tube. While investigating the cause for such great differences in the resistances of the bars, it was found that the resistance altered materially according to the intensity of the light to which they were subjected.

When the bars were fixed in a box with a sliding cover so as to exclude all light, their resistance remained at its highest and was very constant, but immediately upon removal of the box cover, the conductivity increased from 15 to 100 per cent, according to the intensity of the light falling upon the bar. Merely intercepting the light by passing the hand before an ordinary light placed several feet from the bar increased the resistance from 15 to 20 per cent. If the light be intercepted by glass of various colors, the resistance varies according to the amount of light passing through the glass.

Selenium cells have numerous industrial applications such as in the optophone, an apparatus invented by D'Albe by which the blind may read ordinary type by ear; the self-lighting buoy; control apparatus for chimney draft; subway, tunnel, and vehicular-tube ventilation control; control of progress in sulphuric acid manufacture by the contact process; and various other minor uses.[5]

The selenium cell, however, can only be used where the recovery of its absolute resistance upon change from light to dark does not have to be instantaneous. Where this change must be instantaneous, other cells such as the potassium photoelectric cell or the copper oxide cell are used.

During recent years selenium cells have been considerably improved and several makes are now on the market, where the inertia has been reduced to a minimum, and the possibility of using selenium cells for television purposes is again being investigated.

Another unusual use of selenium is that for flameproofing electric switchboard cables. The cables behind the switchboards of generating and distributing stations are apt to accumulate dust, and this occasionally produces short circuits which when heavy currents are carried may set fire to parts of the cable covering.

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5 Wein, Samuel, Selenium Cells and How They are Made. Progress Pub. Co., New York, 1919, 32 pp.

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Cables treated with a thin layer of metallic selenium, however, are made flameproof to a remarkable extent. One part of selenium will flameproof 3.6 parts of cotton and 10 parts of rubber to such an extent that if the treated cable be held in a flame until the characteristic livid blue flame of burning selenium is observed, the burning material is immediately extinguished upon removal from the flame. It has been found that 1 pound of selenium will protect a mile of ordinary cotton-covered wire.[6]

The principal use of selenium and its compounds at present is as a decolorizer in the glass industry and for the production of ruby glass (sailing signals, auto tail-lights, railroad signal lights, etc.) and ruby glazes in the ceramic industry. Its principal use in the glass industry is to offset the greenish tint which is caused by traces of iron in the glass sand. Manganese dioxide has been used for this same purpose but does not work so well in a tank furnace. Selenium, moreover, is less sensitive to changes in the furnace atmosphere. The selenium is added, both as the element and as sodium selenite, in the proportion of about one-half ounce to 1,000 pounds of sand, together with one-sixth to one-eighth of its weight of cobalt oxide, to correct the slight muddiness which remains after selenium decolorization. Selenium requires the presence of arsenious oxide to render it thoroughly effective. It has been found that sodium selenite is far more effective as a decolorizer than metallic selenium, even when allowance is made for the selenium lost by volatilization. If too much selenium is added a yellow or ruby color may develop.

In the manufacture of ruby glass, selenium is used extensively, either in the form of the element or as the selenite in conjunction with a reducing agent such as arsenious oxide; red lead and gold chloride, however, are also used for the same purpose. When selenium is used the glass batch must be treated by an elaborate series of heatings and coolings in order to develop the ruby color.

Another use for selenium which may become of importance is as a solvent. It has been stated that selenium in the form of selenium oxychloride is one of the most powerful solvents known. Synthetic phenolic resins, such as red manol or bakelite, which are used for many industrial purposes and have hitherto been regarded as totally insoluble are now readily dissolved by selenium oxychloride.[7] The solvent, itself, is a heavy, nearly colorless liquid and can be readily shipped in certain types of containers.

Considerable research work has been carried on in the past concerning the use of selenium as a vulcanizing and accelerating agent in the manufacture of rubber. According to Webster Norris:[8]

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6 Dyson, G. M., Extraction and Uses of Selenium. Chem. Age, London, March 3, 1928, p. 19.

7 Lenher, Victor, Occurrence, Chemistry and Uses of Selenium and Tellurium. A Trans. Am. Inst. Min. and Met. Eng., No. 1198-N, Feb., 1923, 20 pp.

8 Norris, Webster, Sulphur and Selenium. India Rubber World, July 1, 1928, p. 61. Copyright, 1928, by W. Norris.

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"Selenium, when mixed with rubber and heated under vulcanizing conditions, results in a product somewhat like that obtained with sulphur. Selenium and sulphur are allied in vulcanizing properties and may be used together very successfully. If the usual organic accelerators are also present, a very tough, rigid, high modulus cure results. In addition to the increased rigidity and modulus, greatly improved abrasion qualities are produced by selenium. Compounds vulcanized to a correct cure with selenium and sulphur age very well, and especially when they contain an antioxident.

"Several patents (United States patents 1,249,272; 1,364,055; 1,622,534; 1,622,535 and 1,622,536) have been granted on the use of selenium and selenium compounds in rubber. The compound known as selenium diethyldithio carbonate is very similar in action to Tuads or tetramethylthiuram disulphide. When used in sufficient quantity it acts as a vulcanizing agent similar to sulphur.

"Vandex is a trade name for mineral selenium specially prepared and refined for the vulcanization of rubber. The chief advantages obtained by selenium vulcanization are the increase in abrasion resistance of high-grade compounds and the possibility of using even larger quantities of reclaim rubber without sacrificing wear-resisting qualities."

The use of selenium in the rubber industry is increasing, and it is estimated that in 1929 about 100,000 pounds of selenium were used in this industry. The potential demand for selenium, if the use of selenium is adopted by the entire rubber industry, is far greater than the copper refineries can furnish.

Fine-drawn wire of selenium and tellurium made by the Taylor process is finding some commercial applications. This wire may be drawn to diameters as small as 1 millimeter to 1 micron.[9]

TESTS FOR IDENTIFICATION[10]

One of the simplest tests for selenium is to heat a little of the mineral on charcoal before the blowpipe. If containing selenium, it will emit a strong odor of decayed horse-radish.

Another test is to heat a little of the mineral on charcoal in the oxidizing flame. A white sublimate is formed, which when treated with stannous chloride becomes red, owing to the reduction of the oxide to metallic selenium.

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9 Skowronski, S., Selenium and Tellurium. The Mineral Industry, New York, vol. 36, 1927, p. 525.

10 Cahan, Edward, and Wooton, Wm. Ord, The Mineralogy of the Rarer Metals. London, 1912, p. 88.
Brush, Geo. J. and Penfield, Samuel J., Manual of Determinative Mineralogy. New York, 1901, p. 107.

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In the open tube, selenium yields a white oxide, SeO_2, which usually crystallizes in radiating prisms on the sides of the glass and is reddened by an admixture of finely divided selenium.

In the closed tube, selenium volatilizes from some of its compounds and condenses as black globules fused against the glass, but where the globules are very minute, they transmit some light and cause the thinnest part of the sublimate to appear red or brown. Owing to the air in the tube, a little oxide, SeO_2, may form, which crystallizes on the glass above the selenium.

HISTORY

In 1817, some nineteen years after the discovery of tellurium, John Jacob Berzelius and Gotlieb Gahn observed during the course of their examination of methods of sulphuric acid manufacture at Gripsholm, Sweden, a sediment in the acid. Before the blow-pipe this sediment, partly reddish and partly clear brown in color, gave off a peculiar odor, like that attributed by Klaproth to tellurium. Berzelius named the new element selenium, from the Greek work "selenos," the moon, in contradistinction to tellurium.

OCCURRENCE AND MINERALS

Selenium, although fairly widely distributed, is not very abundant in nature. It is found associated with its sister element, sulphur. In fact, deposits of native sulphur (notably those in the Hipari Islands north of Sicily, at Kilanca on Kanai, the northernmost island of the Hawaiian group, and Japan) sometimes show a readily distinguishable red-brown coloration, which is caused by a small content of selenium.

The sulphides of the heavy metals likewise are often accompanies by selenium and tellurium, presumably in the form of selenides and tellurides. Certain iron pyrite, such as that from Greece, Spain, Germany, and from the Scandinavian peninsula, contains some selenium. Both the German (notably the Mansfeld mine in the Harz Mountains) and the Scandinavian pyrite yield selenium. The selenium is not, of course, the object of the metallurgical operations, but it is recovered commercially with nickel and molybdenum as by-products from the smelting operations which have as their main object the production of copper and of sulphuric acid.

Selenium has been found in meteoric iron and in the mineral water from La Roche-Posay.

The following is an incomplete list of minerals containing selenium:-[11]

11 Cahan, E., and Wooton, Wm. Ord, The Mineralogy of the Rarer Metals. London, 1912, pp. 89 - 94.

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List of selenium-bearing minerals

Minerals	Chemical symbol	Per cent of selenium
Selen-sulphur (Volcanite)	- -	35-66
Frenzelite (Guanjuatite) (Castillite) (Selenobis muthite)	Bi_2Se_3	24-34
Clausthalite	$PbSe_x$	27-28
Naumannite	Ag_2Se	26
Berzelianite (Berzeline)	Cu_2Se	39
Lehrbachite	$HgPbSe_x$	26
Eucairite	$AgCuSe_x$	31
Zorgite (Raphanosmite)	$CuPbSe_x$	29-48
Tiemannite	HgSe	25-29
Onofrite	Hg(SeS)	4-6
Galenobis muthite	$PbBi_2S_4$	0-14
Rittingerite	(Silver arseno-selenide)	
Selenolite	SeO_2	
Chalcomenite	$CuSeO_3$, $2H_2O$	35
Molybdomenite	(Lead selenite)	
Cobaltomenite	(Impure cobalt selenite)	
Kerstenite	(Lead-copper selenite)	
Crookesite	$(TlAgCu)_2$ Se	30-33

PREPARATION

The earliest method of preparation of selenium to be used on anything like a large scale was the burning of lead chamber sludge with the formation of selenium dioxide, which may be readily condensed in the form of white crystals. The selenium was then dissolved in water and precipitated by sulphur dioxide. This method is not, in use to-day, however, due to the exceptionally large loss (30 per cent) of selenium and also because the product invariably contains about 0.5 per cent of lead which destroys its photoelectric sensitivity and renders it unfit for apparatus utilizing this property. For these reasons other methods have been devised for the extraction of the element.

In the refining of copper in the United States, selenium and tellurium are found in the slime combined with silver and copper to form the respective selenides and tellurides. During the ordinary furnace treatment in the cupel or doré furnaces, part of the selenium is condensed in the flue system, or caught in the solutions and sludges of the cottrell precipitation. The flue dust and sludges are roasted carefully at a low temperature, the selenium dioxide of the flue dust sublimes, and the metallic selenium is converted into the dioxide, which is caught in the flues and is known as "selenium whispers." This deposit is

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dissolved in water, acidulated with sulphuric acid, and the selenium precipitated with sulphur dioxide gas. The major part of the tellurium and some of the selenium remains with the silver in the molten charge and must be removed with an alkali oxidizing flux; a mixture of soda-ash or caustic soda with sodium nitrate is used for this purpose. The selenium and tellurium are then practically completely removed from the silver, chiefly as sodium selenite or selenate and tellurite or tellurate compounds which are soluble in water. The alkaline slugs are leached with water, which dissolves almost all the selenium and tellurium compounds; and on neutralizing the liquors with sulphuric acid, insoluble tellurium oxide is precipitated and filtered. The selenium in the liquors or filtrate is precipitated with sulphur dioxide gas, while the tellurium oxide is either sold as such, or reduced to metal by heating with carbon or by re-dissolving with strong acid and precipitating metallic tellurium with sulphur dioxide gas.

The red amorphous selenium is filtered and dried, by which operation it turns black, then is pulverized and screened to pass completely through an 80-mesh sieve.

The selenium and tellurium of commerce usually analyzes over 99 per cent, the major impurity being a little selenium in the tellurium and a little tellurium in the selenium.

Other methods have been recently described in an English Trade Journal.[12] The wet method for the extraction of selenium from chamber sludge, may be divided into three groups, involving (1) permanganate, (2) chloride, and (3) sulphur trioxide, all of which act as oxidizing agents.

In the permanganate process the sludge is treated in diluted sulphuric acid with potassium permanganate; this oxidizes the selenium to selenious acid and converts the lead to lead sulphate, which is insoluble.

In the chlorate method, potassium or sodium chlorate is used as the oxidizing agent instead of permanganate, the acid used is slightly more diluted to avoid the risk of explosion, and the chlorate is added more slowly. The whole of the reaction mixture is heated to about 70° C. in order to make the selenium dissolve more rapidly. The end of the reaction can be judged by the color of the solution after a test sample has been boiled; if the solution is colorless or pale green, the iron present is still in the ferrous state and further oxidation is necessary.

Recently it has been found that sulphur trioxide is the most suitable and least costly oxidizing agent for the extraction of selenium.[13] The sludge is spread over the bottom of a large lead-lined digestor, oleum containing 20 per cent of SO_3 is added, and the mixture is warmed. Under these circumstances the reaction between SeO_2 and SO_2 is reversible and in the presence of an excess of sulphur trioxide, selenium can be oxidized to the dioxide.

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12 Dyson, G. M., Extraction and Uses of Selenium. Chem. Age., London, March 3, 1928, p. 18.

13 Dyson, G. M., Work cited.

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Selenium extracted by either of these three processes varies considerably in purity. If great care is taken, extraction by the chlorate method will result in a metal containing as high as 95 per cent of selenium, while in the sulphur trioxide process the purity is about 85 per cent.

Distillation has proved to be the only satisfactory method of purification. Since selenium boils at about 680° C., the water and any free sulphuric acid distil over long before the selenium, the other impurities remaining behind. The process of distillation is effected in a cylindrical retort which is kept at a temperature of about 360° C. After the charge of selenium is placed in the retort it is brought to the boiling point in about three hours. During the next nine hours the selenium distils over, is condensed to the liquid state, and then cast into ingots. About 30 to 40 per cent of the selenium remains behind in the residue and refuses to distil. The percentage of yield is affected entirely by the nature of the impurities. If the impurity is mainly calcium sulphate, more selenium remains behind than when the impurities are lead sulphate and oxide.

DOMESTIC PRODUCTION AND SALES

The production of selenium in the United States depends entirely upon the rather limited and uncertain demand for the product. Up to within recent years the output of selenium has been very erratic. Since 1922, however, there has been an exceptional growth in the sales of selenium. In that year 123,565 pounds was sold at a value of $177,542, an average of $1.44 a pound. By 1925 the sales amounted to 194,007 pounds, valued at $330,637, an average of $1.70 a pound. There was a further increase in the sales of selenium in 1926 to 252,312 pounds, valued at $438,132, or an average of $1.74 a pound; and in 1927, the latest year for which figures are available, sales increased to 284,508 pounds valued at $491,996, or an average of $1.73 a pound.

With the increase in the amount of selenium sold there was likewise an increase in the amount of selenium held in stock at the refineries, indicating that production has been steadily increasing since 1922. The stocks on hand at the end of 1927 were 158,494 pounds.

The following Table 3 shows the sale of selenium from 1910 to 1927, and stocks on hand at the end of each year, so far as figures are available.

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Table 3. - Sales of selenium and stocks on hand at end of year, 1910-1927

(in pounds)

Year	Sales	Value	Price per pound	Stocks at end of year
1910	10,674	$ 35,000	$3.28	- - -
1911	(1)	(1)	(1)	(1)
1912	(1)	(1)	(1)	(1)
1913	29,097	46,900	1.61	- - -
1914	22,867	34,277	1.50	- - -
1915	(1)	(1)	(1)	(1)
1916	(1)	(1)	(1)	(1)
1917	39,630	70,000	1.77	- - -
1918	103,694	206,540	1.99	14,500
1919	60,025	125,966	2.10	- - -
1920	92,141	175,508	1.90	- - -
1921	55,978	89,148	1.59	- - -
1922	123,565	177,542	1.44	- - -
1923	127,174	237,196	1.86	677
1924	153,762	286,066	1.86	48,419
1925	194,007	330,637	1.70	61,775
1926	252,312	438,132	1.74	72,374
1927	284,508	491,996	1.73	158,494

1 Not available.

IMPORTS AND EXPORTS

Table 4 shows the imports of selenium and selenium salts into the United States for the years 1913 to 1928, inclusive. Prior to 1921 the quantity of selenium imported was not recorded, but since that date it has fluctuated considerably, though with a strong tendency to increase. The larger part of the selenium and its salts imported into this country comes from Germany, though Mexico also contributes a substantial quantity. The selenium recovered from the Japanese copper refineries is marketed in Europe, but some of it may find its way to the United States.

There is a fairly large export trade in selenium and its salts, but it is not separately classified in the reports of the Department of Commerce.

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Table 4. - Selenium and selenium salts imported for consumption in the United States, 1913-1928

Year	Quantity, pounds	Value
1913	(1)	$ 320
1914	(1)	43
1915	(1)	59
1916	(1)	302
1917	(1)	2,236
1918	- -	- -
1919	(1)	25,866
1920	- -	- -
1921	1,106	2,099
1922	1,652	2,530
1923	940	1,653
1924	300	606
1925	5,807	10,582
1926	18,885	34,680
1927	15,286	28,199
1928	18,622	33,998

1 Total quantity not reported.

MARKET AND PRICES

Selenium is generally sold in the form of an amorphous powder, approximately 99 per cent pure. Small quantities of selenium in the form of cake and sticks, as well as sodium selenite, selenous acid, and selenium dioxide are sold. The powder will practically all pass 80 mesh, though it also may be had as fine as 200 mesh. It is put up in tins containing 15 and 25 pounds and packed in wooden boxes of four or eight cans. Like tellurium it is sold in lots of 100 pounds or multiples thereof.[14]

Table 5 shows the monthly prices for selenium (black, powdered amorphous, 99.5 per cent pure) per pound for the years 1913 and 1920 to 1929. The average price over a period of years possesses little significance, as the industry is in a process of evolution. It is difficult to forecast future prices from prices which have prevailed in the past except that it is probably not profitable to produce selenium at a figure much lower than $2 a pound. The price of selenium has not fluctuated with demand but is priced by producers in accordance with their costs of production. Most of the relatively small fluctuations as shown in the table may be the result of import sales.

14 Colcord, F. F., Selenium and Tellurium. The Marketing of Metals and Minerals, Spurr, J. E., and Wormser, F. E., New York, 1925, p. 167.

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Table 5. - Monthly prices of selenium[1]

(Black, powdered, amorphous, 99.5 per cent pure, per pound)

	1913	1920	1921	1922	1923	1924	1925	1926	1927	1928	1929
Jan.	$ -	$ -	$2.00-2.25	$2.00-2.25	$2.00	$2.10	$2.20	$1.95	$1.90-2.00	$1.90-2.00	$2.25
Feb.	-	-	2.00-2.25	2.00-2.25	2.15	2.10	2.20	1.95	1.90-2.00	1.90-2.00	2.25
Mch.	-	-	2.00-2.25	2.00-2.25	2.15	2.10	2.20	1.95	1.90-2.00	2.25	2.25
Apr.	-	1.75-2.00	2.00-2.25	2.00-2.25	2.10	2.10	2.20	1.95	1.90-2.00	2.25	2.25
May	-	1.75-2.00	2.00-2.25	2.00-2.25	2.10	2.10	2.20	1.95	1.90-2.00	2.25	2.25
June	-	1.75-2.00	2.00-2.25	2.00-2.25	2.10	2.10	2.20	2.00	1.90-2.00	2.25	2.25
July	2.75-3.25	1.75-2.00	2.00-2.25	1.75-1.85	2.10	2.10	2.10	2.00	1.90-2.00	2.25	2.25
Aug.	-	2.00-2.25	2.00-2.25	1.75-1.85	2.10	2.10	2.10	2.00	1.90-2.00	2.25	2.25
Sept.	2.75-3.25	2.00-2.25	2.00-2.25	1.80-1.90	2.10	2.10	2.15	2.00	1.90-2.00	2.25	2.25
Oct.	2.75-3.25	2.00-2.25	2.00-2.25	1.80-1.90	2.10	2.10	2.15	2.00	1.90-2.00	2.25	2.00
Nov.	3.00-3.25	2.00-2.25	2.00-2.25	1.90	2.10	2.10	2.15	2.00	1.90-2.00	2.25	2.00
Dec.	3.00-3.25	2.00-2.25	2.00-2.25	1.90	2.10	2.10	2.00	1.90-2.00	1.90-2.00	2.25	2.00
Average	3.12	2.01	2.25	1.98	2.10	2.10	2.15	1.97	1.95	2.20	2.18

1 Engeneering and Mining Journal.

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TELLURIUM

DESCRIPTION AND PROPERTIES

Although chemically resembling sulphur and selenium, tellurium more closely recalls antimony in appearance and crystalline states. Amorphous and colloidal varieties, however, also exist.

Tellurium is a silver-white, lustrous, brittle, metallic-looking substance which crystallizes in hexagonal rhombohedra, isomorphous with sulphur and selenium. The specific gravity is given as 6.25 but the density may vary considerably, depending especially upon the temperature. Tellurium melts at 452° C., boils at a red heat, and volatilizes readily when heated in a stream of oxygen. In an almost perfect vacuum it boils at 478° C. The vapor of tellurium is pale yellow at low temperatures, but becomes deep red at 1,250° C., and again pale yellow at 1,350° C. when it consists of diatomic molecules.[15]

Tellurium is a poor conductor of heat and electricity, and its electrical conductivity, unlike that of selenium, is independent of the degree of illumination.

In the periodic chart of D. I. Mendeléef, tellurium by virtue of its chemical and physical properties falls naturally in Column VI with oxygen, sulphur, and selenium. Iodine is even more closely related with the members of the halogen group in Column VII. The generally accepted atomic weight of tellurium, however, is 127.5 and that of iodine is 126.9, indicating that their relative positions should be reversed. The general usefulness of the periodic table has been demonstrated over and over again, but this apparent anomaly which is much more serious than the other exceptions (argon-potassium and cobalt-nickel) remains unexplained.

USES

Metallic tellurium has only slight industrial application. It is used as a crystal detector or dry rectifier in radio work; as a coloring agent in certain glass and ceramic wares; in photography; to give silverware a black finish; and, in the form of diethyl telluride, as an antiknock compound in gasoline for internalcombustion engines.

The use of tellurium in crystal detector sets in radio never assumed important proportions, though for a while the radio industry took what little was sold. In the reflex circuit it was discovered that a rectifier of zincite and tellurium was unsurpassed. Providing the tellurium is not brushed roughly across the surface of the zincite, this detector retains its sensitivity almost indefinitely. Practically all points on the surface are equally sensitive, which is a real advantage over many forms of crystals. With the advent of the radio vacuum-tube set, the use of tellurium for this purpose ceased entirely.

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15 Thorpe, Edward, A Dictionary of Applied Chemistry. Vol. 6, London, 1926, p. 721.

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Tellurium is used for producing blue and brown glass and glazes and the sulphide is used for producing a pink color on porcelain.

In photography a solution of tellurium dissolved in a sodium sulphide solution is used in the toning or coloring baths for photographic prints to give them a brownish tint.

A solution of tellurium oxide in hydrochloric acid is used as a dip for silverware to give a black finish. Although the amount consumed may not be large, this use constitutes one of the few commercial applications of tellurium.

The use of 0.2 per cent diethyl telluride in gasoline imparts certain anti-knock qualities to the fuel and is said to eliminate carbon deposits, greatly increasing the efficiency of motors designed to operate on very high compression.[16] A special type of engine is said to be required to produce these results. Tetraethyl lead and similar compounds, however, have been found to be almost as satisfactory, and as they are cheaper than diethyl telluride, are ordinarily used instead.

The fungicidal properties of the tellurites have been investigated rather extensively, but they appear to be less active for such purpose than the selenites.

The principal immediate outlets for tellurium are in medicinal chemistry and in metallurgy. In medicinal chemistry it has been found that the compounds of tellurium have a certain bactericidal activity which may in the future make them of importance.

Considerable study has been carried on in the past concerning the action of tellurium in aluminum-copper-tellurium alloys. Sisco and Whitmore[17] state that:-

> "From a commercial standpoint the alloys of aluminum-copper-tellurium are, however, of little practical value. Tellurium is insoluble in molten aluminum and as aluminum telluride is removed almost quantitatively from the molten alloy as slag. The traces of tellurium that are left in the metal evidently segregate, and although .. they have little effect on the structure, they exercise a particularly harmful effect upon the physical properties, reducing the strength and ductility in a marked degree."

At present, studies are being made concerning the effect of tellurium in steel, especially the machining qualities of tellurium-steel.

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16 Lenher, Victor, Occurrence, Chemistry and Uses of Selenium and Tellurium. Trans, Am. Inst. Min. and Met. Eng., No. 1198-N, Feb., 1923, 20 pp.

17 Sisco, F. T., and Whitmore, M. R., Properties and Structure of Some Alloys of Aluminum-Copper-Tellurium. Ind. and Eng. Chem., vol. 16, Aug. 1, 1924, p. 839.

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Dr. G. B. Waterhouse and I. N. Zavarine have investigated the properties of steel containing tellurium and found that steel with 0.12 per cent tellurium showed the presence of a nonmetallic constituent, probably a telluride, closely associated with manganese sulphide.[18] When the steel was forged, the telluride did not break up, but elongated fully as well if not better than manganese sulphide. The steel, however, was lower in ductility than normal steel without tellurium. The recommendation was made that further investigation should be made to find whether tellurium could be substituted for sulphur in the free cutting or free machining of steel.

TESTS FOR IDENTIFICATION[19]

A delicate test for tellurium or the tellurides may be made by heating a little of the finely powdered mineral in a test tube with about 5 c.c. of concentrated sulphuric acid, which assumes a reddish-violet color. After cooling, if water is added, the color disappears and a grayish-black precipitate of tellurium is thrown down.

Another test is to heat a little of the substance in a test tube. It will sublime and finally fuse to colorless, transparent drops of the oxide (TeO_2). If tellurium is heated on charcoal, it volatilizes with a white coat having a red or yellow border.

Tellurium will turn silver black, if a little of it is powdered, mixed with sodium carbonate and fused in a reducing flame, and then placed upon the silver in a moistened condition.

HISTORY

In 1782 Müller von Reichenstein suspected the presence of a new metal in an auriferous mineral from the Mariahilf mine near Zalethna in the Fatzburg Mountains of Transylvania. Tellurium was isolated from this mineral by Kitaibel in 1789, and in 1798 the existence of the new element was confirmed by Klaproth, who gave it the name of tellurium, from the Greek work "tellus", the earth.

OCCURRENCES AND MINERALS

Tellurium occurs native in small quantities, associated with silver and gold, but it is usually found combined with these or other metals as tellurides.

The following is a partial list of tellurium-bearing minerals:[20]

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18 Waterhouse, G. B. and Zavarine, I. N., Properties of Steel Containing Tellurium. Iron Age, vol. 112, No. 23, 1923, p. 1576.

19 Brush, Geo. J., and Penfield, Samuel J., Manual of Determinative Mineralogy. New York, 1901, pp. 124-125.

20 Cahan, E., and Wooton, Wm. Ord, The Mineralogy of the Rarer Metals. London, 1912, pp. 97-100.

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List of tellurium-bearing minerals

Mineral	Chemical Symbol	Per cent of Te.
Native tellurium	Te	93-97
Silver telluride	Ag_2Te	
Tetradymite	$Bi_2(TeS)_3$	39-49
(Joseite)		
(Wehrlite)		
Grunlingite	Bi_4TeS_3	12-13
Melovite	Ni_2Te_3	23-76
Tapalpite	$3Ag_2(STe)$, $Bi_2(STe)_3$	20-24
Tellurite	TeO_2	79-80
Montanite	$Bi_2(OH)_4 Te O_6$	17-20
Emmonsite	(Hydrated iron tellurite)	59-60
Durdenite	$Fe_2(TeO_3)_3$, $4H_2O$	42-57
Ferrotellurite	$FeTe O_4$	
Magvolite	$Hg_2 Te O_4$	
Slutzite	$Ag_4 Te$	22-23
Hessite	$Ag_2 Te$	37-44
Petzite	$(Au Ag)_2 Te$	32-35
Altaite	Pb Te	37-38
Coloradoite	HgTe	38-39
Sylvanite	(Au Ag) Te_2	58-62
(Graphic tellurium)		
(White tellurium)		
Krennerite	(Au Ag) Te_x	38-59
(Bunsenine)		
Muthmannite	(Au Ag) Te	46-47
Calaverite	(Au Ag) Te_2	56-58
Nagyagite	$(Au Pb)_2(TeSSb)_3$	15-31
(Elasmose)		
(Black tellurium)		
(Tellurium glance)		
Kalroorlite	$Hg Au_2 Ag_6 Te_6$	37-56
Mullerine	Au Ag Pb Te_x	44-55
Rickardite	$Cu_4 Te_3$	59-60
Coolgardite	(Au Ag Hg) Te_x	51-56

Of the minerals listed in the foregoing table only silver telluride (Ag_2Te) is used for the production of commercial tellurium. In Europe it is found distributed among various deposits, and this material, "Tellurreicherz" contains about 4 to 5 per cent silver telluride.

As previously noted, tellurium is recovered mainly in the United States from the anode slime obtained in the electrolytic refining of copper and lead. These slimes, especially from the copper refineries, also contain gold, silver, and some of the platinum metals, as well as selenium.[21]

21 Clevenger, G. H., Tellurium and Selenium, The Useless Elements. Min. and Met. vol. 4, Jan., 1923, pp. 15-16.

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PREPARATION

The method of extraction of tellurium from copper or lead anode mud is comparatively simple. In the United States it is recovered along with selenium. The insoluble tellurium oxide is obtained from the treatment of the alkaline selenium. The tellurium slags then may be reduced by carbon to metallic tellurium, of the slags may be dissolved in an excess of acid and precipitated with sulphur dioxide gas.

According to Mathers and Turner:[22]

> "Tellurium can be electrodeposited in a firm, smooth condition upon lead cathodes from solutions of tellurium dioxide in mixtures of hydrofluoric and sulphuric acid. Solutions of tellurium dioxide in nitric or in hydrochloric acid give much less satisfactory deposits. This results in a metallic tellurium free from selenium and therefore may be used for refining tellurium."

According to an English trade journal there are several other ways of preparing tellurium, but these methods are not in use in the United States.[23]

The copper or lead sludge is roasted in a strong current of air to form tellurium dioxide deposited in the flues and cooling chambers as minute white crystals, which, in the case of copper slimes, is almost invariably contaminated with arsenic and antimony oxides. This crude oxide is readily reduced to tellurium by smelting with charcoal at a low temperature.[24]

In the extraction of tellurium from silver telluride (Ag_2Te), the tellurium is regarded as a liability rather than an asset, and it is for the recovery of silver that the extraction operations are carried out. If silver telluride is used, the mineral is heated with concentrated sulphuric acid until no more sulphur dioxide is evolved. The solution is decanted from the unsoluble residue, diluted with water, and treated with hydrochloric acid to precipitate the silver. The tellurium is precipitated from the filtrate by sulphur dioxide.[25] Tellurium prepared by either of these two methods is impure, and seldom contains more than 72 to 85 per cent of the element. It can be purified in several ways: By fusion with potassium nitrate and conversion to potassium tellurate, which can be dissolved in water and the tellurium recovered by sulphur dioxide precipitation; by solution in nitric acid, followed by recrystallization of the basic nitrate so formed, and reconverting to the metal by smelting with charcoal; or by vacuum distillation. The last method is deemed the best, despite the fact that only about 60 per cent of the tellurium distills over, the remainder being kept back in the residues.

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22 Mathers, F. C., and Turner, H. L., Electrodeposition of Tellurium. Trans. Am. Electrochem. Soc., vol. 54, 1928, pp. 293-302.

23 Dyson, G. M., The Production and Uses of Tellurium. Chem. Age, London, Sept. 1, 1928, p. 17.

24 Dyson, G. M., The Production and Uses of Tellurium. Chem. Age, London, Sept. 1, 1928, p. 17.

25 Ibid.

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DOMESTIC PRODUCTION AND SALES

While there is only a small industrial application for tellurium in the United States, from 1,000 to 2,000 pounds are sold annually. The largest producers of tellurium in this country are the Raritan Copper Works at Perth Amboy, N. J., the United States Lead Refinery, Inc., East Chicago, Ind., and the plant of the American Smelting and Refining Co., Omaha, Neb.

During 1923, the first year for which figures are available, a little less than 1,000 pounds of tellurium was made and sold by two producers, the Raritan Copper Works and the U. S. Lead Refinery, Inc. The average price received was $2 a pound. Manufacturers of electrical equipment, electro-plating works, and chemical laboratories bought the largest quantities, while smaller lots of a few pounds each were distributed to laboratories for experimental work.

In 1928 the estimated output was 2,650 pounds, but sales apparently amounted to only 1,060 pounds, valued at $1960 or $1.85 a pound. Available figures for intervening years are given in Table 6, following:

Table 6. - Production and sales of tellurium, and stocks on hand at end of year, 1923-1928

Year	Production, pounds	Sales, pounds	Value	Stocks on hand, pounds
1923	1000 1/	(2)	(2)	(2)
1924	(2)	(2)	(2)	(2)
1925	(2)	(2)	(2)	(2)
1926	917	1106	$2229	1119
1927	1659	1003	1913	2337
1928	2650	1060	1960	(2)

1 Approximately.
2 Not recorded.

MARKET AND PRICES

Tellurium is usually sold as being 99 per cent pure and marketed in the form of slabs and sticks, though it is also available in powder form. Shipments are generally made in 100-pound lots and multiples thereof. Premiums and penalties do not affect the quoted price, and shipments are received upon weights and statement of purity made by the seller.[26] A commercial grade of tellurium oxide and a C. P. grade are also in the market.

Table 2 shows the average monthly price of tellurium as quoted in the Engineering and Mining Journal. The price has shown little variation during the four years from 1924 to 1927, inclusive, the price remaining steady at $2 a pound.

26 Colcord, F. F., Selenium and Tellurium. The Marketing of Metals and Minerals, Spurr, J. E., and Wormser, F. E., New York, 1925, p. 167.

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There is no special marketing problem for tellurium; the price is based on supply and demand and hence little change is possible, as the supply is well in excess of demand.

With the exception of the first two months of 1928, when tellurium was quoted at $1.87 a pound, the price has held more or less steady at $2.25 to $2.70 up to the end of 1929.

Table 7. - Monthly prices of tellurium[1]

(Price per pound)

	1923	1924	1925	1926	1927	1928	1929
Jan.	$1.50-2.00	$2.00	$2.00	$2.00	$2.00	$1.87-	$2.25-2.70
Feb.	3.00	2.00	2.00	2.00	2.00	1.87-	2.25-2.70
Mch.	3.00	2.00	2.00	2.00	2.00	2.25-2.70	2.25-2.70
Apr.	3.00	2.00	2.00	2.00	2.00	2.25-2.70	2.25-2.70
May	3.00	2.00	2.00	2.00	2.00	2.25-2.70	2.25-2.70
June	3.00	2.00	2.00	2.00	2.00	2.25-2.70	2.25-2.70
July	2.00	2.00	2.00	2.00	2.00	2.25-2.70	2.25-2.70
Aug.	2.00	2.00	2.00	2.00	2.00	2.25-2.70	2.25-2.70
Sept.	2.00	2.00	2.00	2.00	2.00	2.25-2.70	2.25-2.70
Oct.	2.00	2.00	2.00	2.00	2.00	2.25-2.70	2.25-2.70
Nov.	2.00	2.00	2.00	2.00	2.00	2.25-2.70	2.25-2.70
Dec.	2.00	2.00	2.00	2.00	2.00	2.25-2.70	2.25-2.70
Average	2.39	2.00	2.00	2.00	2.00	2.18-2.56	2.25-2.70

1 Engineering and Mining Journal.

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